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# Determination of sorption isotherms for Eu, Th, U and Am on the gel layer of corroded HLW glass

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## Abstract

The retention of Eu(III), Th(IV), U(VI) and Am(III) in the alteration layer (gel layer) of precorroded simulated HLW glass is investigated by sorption experiments in water, NaCl and $MgCl_2$ brine as a function of the pH. In water, the sorption behaviour of the four elements shows a strong dependence on the pH and the sorption coefficients ($R_s$) determined reflect the different charges of the three ions and the corresponding sorption properties. The $R_s$ values of Th are the highest values, followed by the $R_s$ values of Eu and Am, which are lower by about a factor of 10 at the respective pH, and finally by the $R_s$ values of U(VI) which are the lowest. The sorption behaviour of the four elements can be described by a Langmuir isotherm for pH values <5. As shown by modelling calculations, the strong increase of the $R_s$ values of Eu and Am, as well as of Th, with increasing pH can be described by the formation of a bidentate surface complex. Above pH 4–6, colloidal particles could be detected. From the concentrations of Nd in the solutions leached from the glass, 'desorption' coefficients ($R_d$) of Nd can be calculated. The $R_d$ values of Nd correspond quite well with the $R_s$ data of the chemically homologue Eu and Am. In NaCl brine the sorption behaviour of Th and U is rather similar to that in water, whereas in $MgCl_2$ brine the sorption of Eu, Am, and U in the gel layer is much lower than in water or NaCl brine. The results of the sorption tests can explain the very low release and solution concentrations of REE and actinides found in corrosion experiments with the radioactive CEA glass R7T7 in NaCl-rich solution under neutral to alkaline conditions.

## 1. Introduction

Chemical durability of inactive and high-active nuclear waste glass and its ability to retain radionuclides within its structure (glass network) have been studied by corrosion experiments with aqueous solutions (water, NaCl and $MgCl_2$ brine). The mechanisms of aqueous corrosion are well known [1]. They include water diffusion into the glass (hydration) and ion exchange with the most mobile network modifier ions (interdiffusion). A reaction zone is created, within which a hydration and $H^+ \leftrightarrow$ alkali metal interdiffusion profile is formed. The hydrated silicate network subsequently dissolves, hydrolysing all the glass component elements (congruent dissolution).

Grambow [2,3] has developed a dissolution/precipitation model (reaction path model) for glass corrosion, where it is assumed that the glass dissolves congruently by a first-order dissolution rate law ($R = R_o(1 - a_{Si}/a^*_{Si})$ with $R$ = dissolution rate, $R_o$ = forward corrosion rate far from Si saturation, $a_{Si} = H_4SiO_4$ activity, and $a^*_{Si} = H_4SiO_4$ activity at saturation). The activity of $H_4SiO_4$ in the solution is the key parameter. From the first-order law, it is expected that the dissolution rate drops to zero at saturation. Many corrosion experiments [4–6] have shown, however, that corrosion decreases by several orders of magnitude from the initial rate, but does not attain zero even under silica-saturated conditions. In corrosion studies using large glass surface area to solution volume ratios ($S/V$), it has been shown that the long-term release of Li and B from the glass into $MgCl_2$-rich solutions under acid conditions (pH ~ 4) follows a square root of time rate law, which is an indication of a diffusion-controlled dissolution process. However, the mechanism of long-term glass corrosion, especially at higher pH values (e.g., in NaCl brine), is not fully understood.

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Many glass constituents and radionuclides are less soluble especially in alkaline media. Their release rates are lower than the glass dissolution rates by several orders of magnitude. Actinides, rare-earth elements, Fe, Al, Zr, and other elements are assumed to be retained in the surface layer (gel layer) of the glass by sorption or by formation of secondary alteration products controlling the solution concentrations. Retention of the various elements, sorption isotherms for radionuclides on the alteration layer, and the solubility of simple phases, solid solutions, and more complex compounds (silicates, molybdates, sulfates, etc.) have not yet been well defined or studied.

## 2. Sorption experiments

To quantify the sorption effect on the elemental release, sorption isotherms of Eu (homologue element for trivalent actinides), Am, Th (homologue for Pu(IV), U(IV) and Np(IV)) and U(VI) were determined using precorroded glass GP WAK1 as substrate. The glass GP WAK1 was developed for the vitrification of the HLLW of the reprocessing plant in Karlsruhe (WAK) [7]. Objectives of the sorption tests are:

- identification of the sorption effect;
- determination of the sorption coefficients ($R_s$) and comparison with the leaching behaviour;
- modelling of sorption.

Sorption studies were performed in deionized water, $MgCl_2$-rich and NaCl-rich solutions at 80°C. Some experiments were performed at ambient temperature (23°C) as well, as a function of the pH. Besides the effect of the pH, the studies should also provide information about the effects of solution contacting time, starting concentration, and temperature.

For preparing precorroded glass samples, samples of 2.5 g glass powder (grain size 200–280 μm) were exposed to 50 ml water ($S/V = 1000\ \mathrm{m}^{-1}$) for 40 days. The tests were performed under atmospheric conditions. The pH of the solution was not controlled during precorrosion and, therefore, the solution pH increased to about 9. After 40 days, aliquots were taken from the leachates and analysed for Si, Li, B, Ca, Mo and Nd. From the concentrations of B and Si, the amount of the alteration layer formed was calculated. After sampling, the pH of the solutions was adjusted to different fixed values (10 values between pH 2 and 10) by addition of either $HNO_3$ or NaOH. The pH values of the solutions were measured with a pH electrode (Ross system) under stirring. Due to the reaction with the glass, the pH of the solutions increases continuously, especially at pH 3–6. Therefore, the pH was daily measured and readjusted to the fixed values. Sorption studies were performed at $10^{-6}$, $10^{-5}$, $10^{-4}$, $5 \times 10^{-4}$ and $10^{-3}$ mol/l of the elements Eu, Th and U. For $^{241}$Am(III) concentrations of $10^{-9}$–$10^{-7}$ mol/l were used. The concentrations were obtained by adding stock solutions (0.5 ml) of these elements to the solutions of the precorrosion experiments.

The concentrations of the four elements in the leachates were determined 1 and 10 days after solution addition, respectively, and in some experiments also after 30 and 50 days. After 10 days, sorption equilibrium was reached in most experiments. For solution analyses, aliquots were taken and filtered through 0.45 μm filters. The filtrates were also passed through an ultrafiltration membrane (pore size 18 Å) to check for colloid formation. The analysis of Eu, Th, and U was performed by ICP-MS, that of $^{241}$Am by γ-spectrometry. The detection limits of the ICP-MS are in the range of 0.02–0.05 μg/l.

## 3. Results and discussion

Results of the sorption experiments are given in the figures in terms of $R_s$ (l/g) values. $R_s$ is calculated from the amount of the element sorbed $C_{\mathrm{sorb}}$, divided by the elemental concentration in the solution $C_{\mathrm{sol}}$ and multiplied by the ratio of the solution volume ($V$) to mass of surface layer ($m$). $C_{\mathrm{sorb}}$ is the difference between the starting concentration in the solution and the concentration analysed (equation):

$$R_s = C_{\mathrm{sorp}}/C_{\mathrm{sol}} \cdot V/m \quad (\mathrm{l/g}). \tag{1}$$

The mass of the surface layer $m$ was calculated from the normalized mass loss of boron minus the normalized mass loss of Si, multiplied by the surface area of the sample and corrected for an assumed layer density of 2 g/cm$^3$ (value between the density of the glass (2.64 g/cm$^3$) and density of the gel layer (1.5–2 g/cm$^3$)). The quantity sorbed on the glass corrosion products and the calculated sorption coefficients $R_s$ were deduced from the decrease of the solution concentration after 10 days. $R_s$ values were calculated for filtered and ultrafiltered solution samples to check for colloid formation.

### 3.1. Sorption behaviour in water

$R_s$ values for Eu(III) at 80°C after 10 days for three starting concentrations of $10^{-6}$, $10^{-5}$ and $10^{-4}$ mol/l Eu as a function of the pH are given in Fig. 1. In the pH range 2–6, the $R_s$ values were found to be independent of the starting concentration. This is a characteristic finding for a ideal sorption process following the Nernst equation ($C_{\mathrm{sorb}} = KC_{\mathrm{sol}}$, see below). In this pH range colloidal particles were not detected. At higher pH, colloid formation could be observed. The Eu concentrations in the 0.45 μm filtered solution samples were

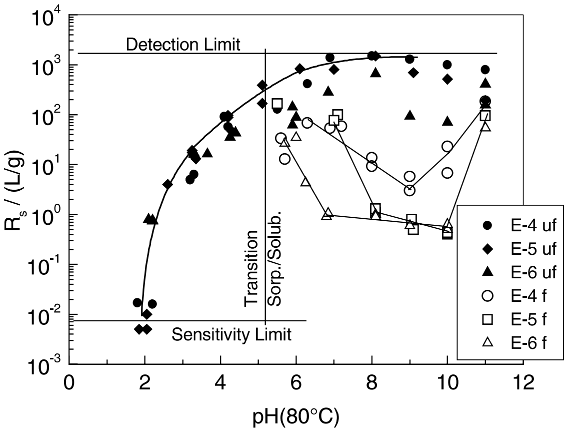

Fig. 1. Sorption coefficients $R_s$ of Eu on glass corrosion products in water at 80°C (uf: ultrafiltrated; f: filtrated solution).

much higher than those in the ultrafiltered solutions. Although $R_s$ values have no physical bearing if colloidal particles are present, the respective values are included in the diagram to illustrate the effect of the colloids.

The next diagram (Fig. 2) shows the sorption edges of Eu, Th, U(VI), and Am at 80°C for a starting concentration of $10^{-4}$ and $10^{-8}$ mol/l (Am). As expected, the $R_s$ values of both trivalent elements Eu and Am agree quite well. The sorption isotherms of the four elements reflect the different charges of the ions and the corresponding sorption properties. The pH edge of Th(IV) is located at the lowest pH values and the $R_s$ values show a strong increase with pH. Above pH 4, $R_s$ values remain constant, as the Th concentrations in the solution are in the range of detection limits of $5 \times 10^{-9}$ mol/l. The $R_s$ values of Eu(III) and Am(III) are considerably lower (~factor 10) at the corresponding pH values. Above pH 6.5, the $R_s$ values of Eu remain constant as the concentrations are below the detection limits ($10^{-8}$ mol/l) as well. Lowest sorption coefficients occur for U(VI). The coefficients are lower than those of Th by about a factor of 100, thus reflecting the lowest charge of the four ions. Above pH 4, the sorption coefficients are constant, the U concentrations in the solution remain here in the range of $10^{-6}$ mol/l. Above pH 8, the $R_s$ values decrease again. This effect can be attributed to the formation of anionic carbonate complexes, as the solutions are in contact with air. Similar to Eu, Th- and U-containing colloidal particles were detected. Above pH 4–6, the $R_s$ values calculated from the concentrations in the 0.45 μm filtered solution samples show a distribution quite similar to that of Eu (see Fig. 1).

The strong increase of the $R_s$ values with pH may be explained by a reaction of the type used by Östhols [8] for modelling the Th sorption on amorphous silica:

$$2{\equiv}\text{SiOH} + \text{Th}^{4+} + \text{H}_2\text{O} \leftrightarrow ({\equiv}\text{SiO})_2\text{Th}^{2+} + 2\text{H}^+. \qquad (2)$$

$2{\equiv}$SiOH denotes a combination of two surface sites on the glass surface, which are close enough to bind a sorbing $\text{Th}^{4+}$ ion. This complexation reaction can explain the strong effect of pH on the Th as well as on the Eu and Am sorption.

During precorrosion of the glass and the following sorption tests, Nd is leached from the glass. From the Nd concentrations in the solution, a desorption coefficient ($R_d$) for Nd can be calculated. These $R_d$ data are included in Fig. 3. As can be seen from the diagram, the $R_d$ values of Nd correspond quite well with the ($R_s$) data of the chemically homologue Eu. Consequently, the retention of REE observed in glass corrosion experiments can be explained by sorption on the alteration layer on the glass surface.

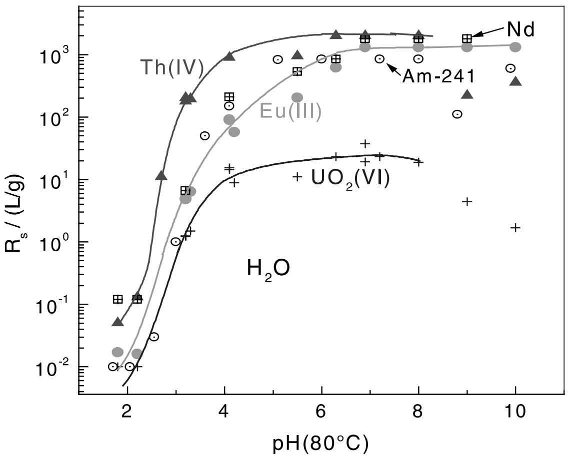

Fig. 2. Sorption coefficients $R_s$ of Eu, Th and U and desorption coefficients $R_d$ for Nd in water at 80°C.

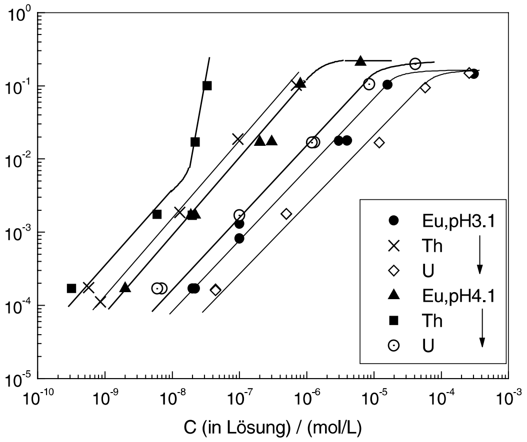

Fig. 3. Sorption isotherms of Eu, Th and U in water at 80°C for pH 3.1 and 4.1.

In Fig. 3 the sorbed concentrations (mol/kg) of Eu, Th and U are plotted versus the concentration in the solution for pH values of 3.1 and 4.1. The sorption isotherms show that the sorbed concentration is about proportional to the solution concentration. Therefore, the sorption behaviour of the three elements can be described by a Langmuir isotherm. In case of low solution concentrations, the Langmuir isotherm (4) assumes the simple linear form

$$C_{\mathrm{sorb}} = K_{\mathrm{ad}} C_{\max} C_{\mathrm{sol}} \tag{3}$$

with $C_{\mathrm{sorb}}$ = metal concentration sorbed (mol/kg), $C_{\mathrm{sol}}$ = metal concentration in solution (mol/l), $K_{\mathrm{ad}}$ = adsorption constant, and $C_{\max}$ = maximum possible sorption. The sorbed metal concentration is proportional to the concentration in solution and in a double-logarithmic presentation the Langmuir isotherms follow straight lines with a slope of one. Even if the number of experimental sorption data is low and the data show a relatively large scattering, it is justified to assume a slope of one for the pH isotherms of Eu, Th and U and to interpret the retention of these elements as a sorption effect (Eq. (3)). As shown in Fig. 3, the sorbed concentrations are not proportional to the solution concentration at high concentrations of Eu and U. From the equation of the Langmuir isotherm,

$$C_{\mathrm{sorb}} = \frac{C_{\max} K_{\mathrm{ads}} C_{\mathrm{sol}}}{1 + K_{\mathrm{ads}} \cdot C_{\mathrm{sol}}}, \tag{4}$$

it follows that the sorbed concentration $C_{\mathrm{sorb}}$ remains constant, if the maximum possible concentration is attained ($C_{\max}$) and all sorption sites are occupied. Therefore, the number of sorption sites can be determined from these sorption isotherms or, if we assume an ion exchange mechanism, the cation exchange capacity (CEC) can be determined. In order to calculate the CEC, some assumptions have to be made. It is supposed that the gel layer has been transformed completely into smectite minerals (smectite has been detected repeatedly in glass surface layers, e.g. by Abdelouas et al. [9]), the CEC should be between 70 and 130 meq/100 g. Indeed, the CEC, or the number of titratable sites, found for the gel layer by surface titration corresponds to about 100 meq/100 g. If we assume that two ions can be sorbed per nm$^2$, the surface area of the gel layer must be higher than the geometric surface area of the glass powder by about a factor of 300–500. In contrast to Eu and U, the sorbed concentration of Th at pH 4.1 shows a sharp increase at about $10^{-8}$ mol/l. This effect can be explained by the precipitation of $Th(OH)_4$, as saturation concentration is attained and, apparently, the amount sorbed increases.

At pH values above pH 4–6, colloidal particles were detected in all sorption experiments. This may be an effect of solubility constraints with respect to amorphous solid phases. To find out whether the concentrations of these elements are controlled by the solubility of solid phases or by sorption/coprecipitation, the concentrations of U in water are plotted versus pH for various starting concentrations in Fig. 4. The concentrations in the solutions increase correspondingly with the starting concentrations, except for the highest U concentration of $10^{-3}$ mol/l. This suggests a sorption effect. The stability limits of U(VI) containing solid phases (schoepite) from the literature [10] are shown schematically in Fig. 4 as well. The solubility limits are well above the concentrations found in the sorption tests at starting concentrations of $\leqslant 10^{-4}$ mol/l U. Obviously, the U concentration in these solutions is controlled by sorption and/or coprecipitation over the entire range of pH, as U-containing colloidal particles are present in the solution. The increase of the U concentration above pH 8 can be explained by the formation of anionic carbonate complexes.

In Fig. 5 the corresponding concentrations of Eu and Am are shown for starting concentrations between $10^{-5}$ and $10^{-3}$ mol/l and $10^{-7}$ mol/l, respectively. Furthermore, the concentration of Nd leached from the glass is indicated. As for U, the concentrations of Am and Eu in the solutions increase in accordance with the starting concentrations. Below pH 7, the Eu and Nd concentrations appear to be controlled by sorption, as the concentrations are outside the stability region of $AmOHCO_3$ (cr), the stable solid phase of the chemically homologue actinide element Am under these conditions [11] (the solubility limits of $Am(OH)_3$ (am) are rather similar to the limits shown in Fig. 5). Above pH 7, the Eu and Nd concentrations are inside or rather near the solubility limit and Eu-containing colloidal particles are

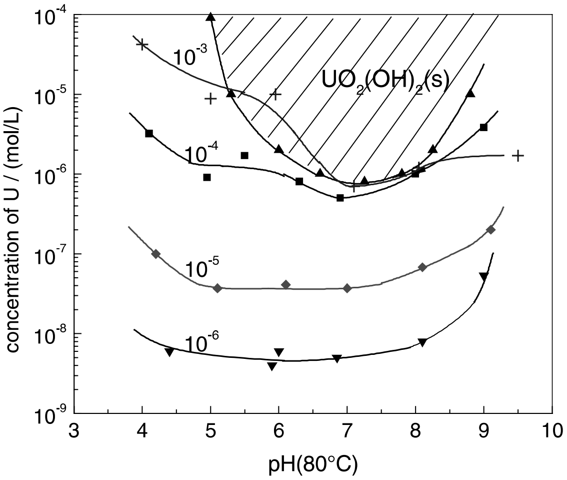

Fig. 4. Concentrations of U as obtained from the sorption tests in water as a function of the pH for various starting concentrations.

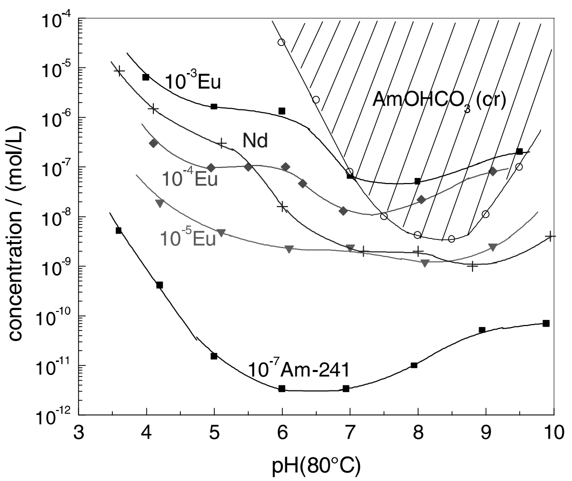

Fig. 5. Concentrations of Eu, Nd and Am as obtained from the sorption tests in water as a function of pH.

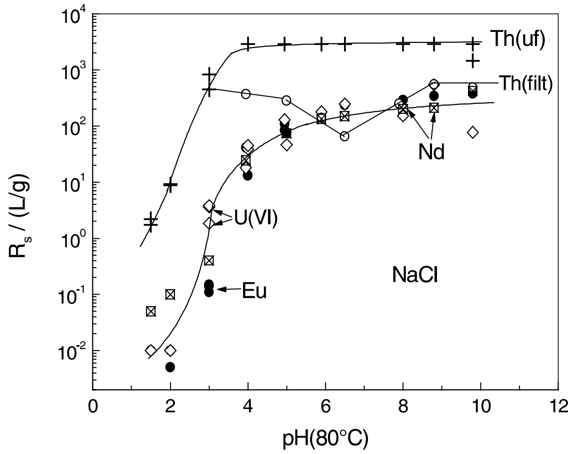

Fig. 6. Sorption coefficients $R_s$ of Eu, Th and U and desorption coefficients $R_d$ for Nd in NaCl brine.

present in the solutions. Therefore, the Eu and Nd concentrations determined in the solutions can be explained by the solubility of solid Me(III) phases (Me = metal). The Am concentrations are far below the stability limits of $AmOHCO_3$ (cr) and $Am(OH)_3$ (am) over the entire range of pH. As above pH 6, Am-containing colloidal particles were detected as well. The Am concentration may be controlled by sorption onto the gel layer and gel layer particles and/or by coprecipitation with, e.g., REE leached out from the glass.

### 3.2. Sorption behaviour in salt solution

To study the sorption behaviour of Eu, Th, U(VI) and Am in concentrated salt solution, sorption studies were performed in NaCl-rich and $MgCl_2$-rich solutions. The glass powder was precorroded in water at 80°C over 40 days (see above). Then, salt was added to the solution to install concentrations of 5.5 mol/l NaCl and 5 mol/l $MgCl_2$ and the pH was adjusted to various fixed values. Three days later, Eu, Th and U(VI) were added. For analytical reasons, only the two higher starting concentrations of $10^{-5}$ and $10^{-4}$ mol/l could be used, as the salt solution samples had to be diluted by at least a factor of 100 for ICP-MS analyses. The Am concentrations in the $MgCl_2$ brine were $10^{-8}$ and $10^{-7}$ mol/l.

The sorption edges in the NaCl-rich solution at 80°C are shown in Fig. 6 for Eu, Th and U at a starting concentration of $10^{-4}$ mol/l as a function of pH. Whereas the sorption coefficients of Th and U are rather similar to those in water, the $R_s$ values of Eu are consistently lower and agree quite well with the sorption coefficients of U. Like in water, the $R_s$ data of Th show a strong increase up to pH 4 and then remain constant, as the Th concentrations are in the range of detection limits. Presumably, solid $Th(OH)_4$ controls the solution concentration and, indeed, colloid formation could be detected above pH 4, the Th concentrations in the filtered solution (450 nm) were much higher than in the ultrafiltered solutions (1.8 nm). Eu- and U-containing colloidal particles could be detected as well, but their amounts were much smaller. The desorption coefficients ($R_d$) of Nd leached from the glass are also shown in the diagram. The $R_d$ values quite smoothly follow the $R_s$ values of Eu (and U) and, therefore, the low concentrations of REE found in long-term experiments in NaCl brine can be explained by sorption onto the alteration layer of the glass.

The sorption behaviour of the four elements in the $MgCl_2$-rich solution is represented in Fig. 7 for the pH range 2–6.5. The pH values are corrected for liquid

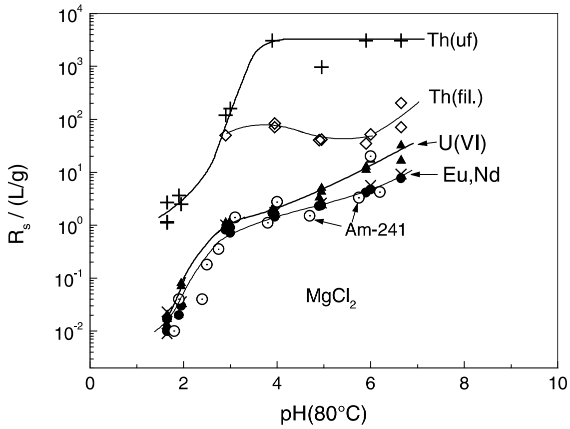

Fig. 7. Sorption coefficients $R_s$ of Eu, Th and U and desorption coefficients $R_d$ for Nd in $MgCl_2$ brine.

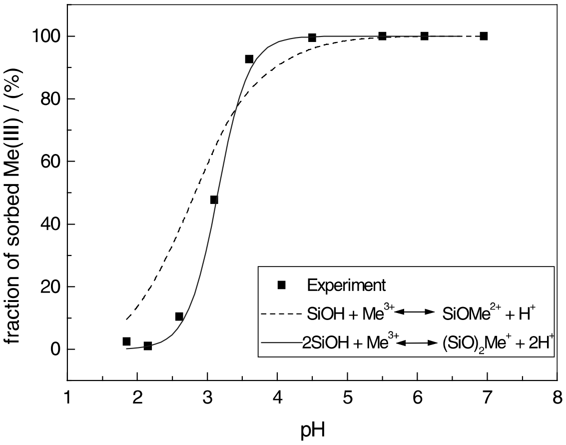

Fig. 8. Calculated and experimental fraction of sorbed $Me^{3+}$ ions in water.

junction potential. In $MgCl_2$-rich brines, the pH cannot be increased to values higher than about 6.5, as precipitation takes place. X-ray diffraction analysis revealed that mainly $MgCl_2 \cdot 6H_2O$ (bishoffite) and small amounts of $Mg(OH)_2$ (brucite) and Mg-chlorid-hydroxide-hydrates precipitate. The sorption behaviour of Th is very similar to that in water and NaCl brine, and Th-bearing colloidal particles could be detected above pH 4 as well (see Fig. 8). In contrast to Th, the retention of Eu, Am and U is much lower than in water or NaCl solution. After an initial sharp rise at low pH, the $R_s$ values increase slowly up to pH 6.5. Eu- and U-bearing colloidal particles were not detected in the $MgCl_2$ brine. Like in water or NaCl brine, the desorption coefficients ($R_d$) of Nd are nearly identical to the $R_s$ values of Eu over the entire range of pH. This low retention of REE, Am and U in the gel layer explains the high release of these elements in the case of HLW-glass corrosion in $MgCl_2$ brines.

The low retention of Eu, Am and U(VI) in $MgCl_2$-rich solutions can be explained by competition of $Mg^{2+}$ ions which occupy the sorption sites in the gel layer because of their high excess. The concentration of the surface sites can be estimated to be about $10^{-3}$ mol/l whereas the $Mg^{2+}$ concentration is 5 mol/l. After addition of Eu, Am and U to the $MgCl_2$-solution, the $UO_2^{2+}$ and $Me^{3+}$ ions may be sorbed by an ion-exchange mechanism. Such a sorption mechanism is supported by the relatively low pH dependence of the $R_s$ values of these elements. In the case of high ionic strength of 10, the chemical activities of the species involved have to be taken into account. For dissolved species the Pitzer formalism is available, but it is not clear how to treat the sorption sites. However, the effect of the high $Mg^{2+}$ concentrations on the sorption behaviour of Me(III) and U(VI) is expected to be much higher than the effect of chloride complexation.

### 3.3. Modelling of Eu and Am sorption in water

The strong dependence of the $R_s$ data on the pH in water can be explained by a surface complexation reaction of Me(III) with the alteration layer. Because of the complex composition of the alteration layer, various sorption sites may exist (≡SiOH, =AlOH, =FeOH, ≡ZrOH, etc.). For modelling the sorption data of Am and Eu determined in water, only the ≡SiOH surface complex was regarded as about 80% of the gel layer consisting of $SiO_2$. In addition, the following assumptions were made for modelling calculations with the code FITEQL (vers. 3.1):

Surface complexation reactions:
Release of protons:

$$\equiv SiOH \leftrightarrow \equiv SiO^- + H^+$$

Acidity constant:

$$\log K = -6.9 \pm 0.1 \quad \text{(Östhols [8])}$$

Surface complexation:

$$1.\quad \equiv SiOH + Am^{3+} \leftrightarrow \equiv SiOAm^{2+} + H^+ \qquad (5)$$

$$2.\quad 2\equiv SiOH + Am^{3+} \leftrightarrow (\equiv SiO)_2Am^+ + 2H^+ \qquad (6)$$

(bidentate surface complex)

Specific surface area of gel layer: ~75 $m^2/g$
Number of sites/$nm^2$: 2
Sorption site species: 1.

For the proton release from the gel layer the stability constant determined by Östhols [8] from studies of Th sorption on amorphous silica was used. For modelling, two different surface complexation reactions were assumed: in the first complexation reaction, $Me^{3+}$ occupies one sorption site, in the 2nd reaction two sites. The specific surface area of the gel layer of about 75 $m^2/g$ can be deduced from surface titration as well as from the maximum sorbed concentration determined by the sorption studies (Fig. 3), assuming two sites/$nm^2$. Furthermore, only one type of sorption site was supposed to exist and Coulomb correction term was not used for calculation.

The results of the modelling calculation together with the experimental results for the Am distribution between solid and liquid phases are shown in Fig. 8. Using the 1st complexation reaction (Eq. (5)), the calculated fractions of sorbed Am increase with the pH to a much smaller extent than the measured fractions. However, the second reaction (Eq. (6)) results in a better agreement between the measured and calculated data. Therefore, the sorption data obtained from Eu and Am indicate the formation of a bidentate surface complex. The complexation constant found to give the best fit to the experimental data is $\log K_s = -0.4$.

## 4. Release of actinides from HLW glass R7T7 in NaCl-rich solution

Static corrosion tests were performed in NaCl-rich solution to study the release of radionuclides from HLW glass R7T7 at 110°C and 190°C, respectively. The measured solution concentrations of actinides are compared with concentrations computed by geochemical modelling calculations using EQ3/6. A thermodynamic equilibrium between the solution and solid phases is assumed and the initial solution composition including all species involved in further reactions is computed. Fig. 9 shows the measured (at 110°C) and computed concentrations of actinides as a function of the glass dissolution progress determined from the boron concentration in solution. The calculations cover a reaction progress between $10^{-6}$ and $10^{-1}$ kg glass/kg $H_2O$ and include the experimental corrosion progress up to 0.011 kg glass/kg $H_2O$. Computations performed for redox potentials with U being in the hexavalent state may explain the rather high concentration by assuming schoepite, $Na_2U_2O_7$ or soddyite to be solubility-controlling solids. For progressive glass dissolution and the computed silica concentration, which is in agreement with the measured data, the precipitation of uranium silicate phases, such as soddyite or haiweeite, is expected. Indeed, silicate phases were observed in some experiments.

Computations for Pu are performed for redox potentials with Pu being in the tetravalent state. The computed concentration of $6 \times 10^{-6}$ mol/kg $H_2O$ is obtained with $Pu(OH)_4$ (am) being the solubility-limiting phase. With the solubilty product taken from Neck [12], Fig. 9 shows a good agreement between the computed results and experimental findings. In case of Am, the measured concentration is about $1 \times 10^{-10}$ mol/kg $H_2O$, whereas the calculations including solid solutions of hydroxides and molybdates yielded data which are higher by three orders of magnitude. If the measured retention coefficients for Eu and Am given in Fig. 3 are used to interpret the discrepancy, a better agreement with the measured Am concentrations is obtained. Therefore, we assume that Am is sorbed onto precipitated amorphous $SiO_2$.

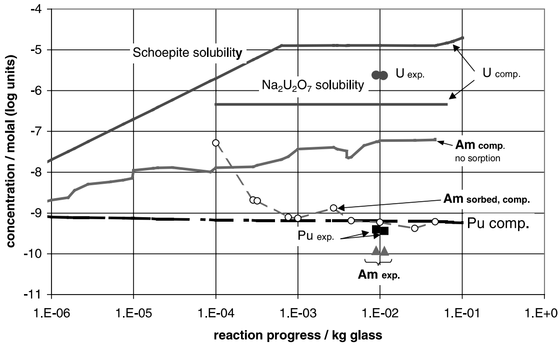

Fig. 9. Computed (lines) and measured (symbols) actinide concentrations released from R7T7 glass in NaCl brine. The line with open circles denotes calculations obtained for Am with sorption at $SiO_2$ (am) being included into the model.

## 5. Summary

Sorption studies were performed with Eu(III), Th(IV), U(VI) and Am(III) using precorroded, simulated HLW glass as the substrate in water and 5.5 M NaCl and 5 M $MgCl_2$ brine. Element sorption was studied as a function of the pH at various starting concentrations. The objectives of the sorption studies were: identification of the sorption effect; determination of the sorption coefficients and comparison with the leaching behaviour (desorption); modelling of sorption.

In water, sorption coefficients ($R_s$) independent of the starting concentrations of Eu, Am, Th and U were found below pH 6. This clearly characterizes the ideal sorption behaviour. The $R_s$ values of the four elements reflect the different charges of the ions and the corresponding sorption properties. The pH edge of Th runs at the lowest pH values, and the $R_s$ values show the strongest increase with pH. Then, the pH edge of Eu and Am follows. Their sorption coefficients are lower than the Th coefficients by about a factor of 10. Finally, the pH edge of U is observed. The $R_s$ values for U are lower than the Th data by about a factor of 100, reflecting the lowest charge of the four ions. Above pH 8, the sorption coefficients of the four elements decrease again due to the formation of anionic carbonate complexes. At low metal concentrations and constant pH, the sorbed concentration is about proportional to the concentration in the solution. Therefore, the sorption behaviour can be described by a Langmuir isotherm. Colloidal particles could be detected at pH values above 4–6. At high starting concentrations, the colloidal particles may consist of amorphous solid phases such as hydroxides and hydroxo-carbonates. At low starting concentration, the concentrations of Eu, Th, U and above all of Am are far below the solubility limit of pure solid phases and, therefore, the colloidal particles detected may have been formed by coprecipitation. From the concentrations of Nd leached out of the glass, desorption coefficients ($R_d$) for Nd can be calculated. These $R_d$ values correspond quite well with the $R_s$ values of Eu and Am. Consequently, the observed high retention of REE and actinides in corrosion tests with HLW glasses can be explained by sorption at the gel layer and/or coprecipitation.

In 5.5 M NaCl brine, the sorption edges of Th and U are rather similar to those in water, whereas the sorption coefficients $R_s$ of Eu are consistently lower and quite similar to the U values. Th-containing colloidal particles could be detected as in water. However, the amounts of Eu- and U-containing colloids are strongly diminished. In the 5 M $MgCl_2$ brine the same sorption/precipitation behaviour of Th is found as in water and NaCl brine. In contrast to Th, the retention of Eu, Am and U(VI) is much lower. Eu- and U-bearing colloidal particles were not detected in the $MgCl_2$ brine. In both brines, the desorption coefficients ($R_d$) of Nd are nearly identical to the $R_s$ values of Eu and Am. The low sorption coefficients of REE, Am and U(VI) observed in the $MgCl_2$ brine explain the high release of REE and actinides, if HLW glasses are corroded in $MgCl_2$-rich solutions. The low retention of Me(III) and U(VI) in $MgCl_2$-rich solutions can be explained by competition of the $Mg^{2+}$ ions which occupy the sorption sites because of their high excess. After addition of Eu, Am and U to the $MgCl_2$ brine, the $UO_2^{2+}$ and $Me^{3+}$ ions may be sorbed by an ion-exchange mechanism. Such a sorption mechanism is supported by the relatively low pH dependence of the $R_s$ values of these elements.

The code FITEQL was used for modelling the sorption behaviour of Eu and Am found in water. It follows from the calculations that the observed strong increase of sorption with pH can be described best by the formation of a bidentate surface complex.

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